PRODUCTION AND CHARACTERIZATION OF SILICON NANOSTRUCTURES FOR THE ADVANCEMENT OF NOVEL ENERGETIC FORMULATIONS

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ABSTRACT

This paper details the synthesis and characterization of Silicon (Si) nanostructured powder with a wide variety of morphologies such as nanoparticles, nanowires, nanotubes etc produced by DC plasma arc discharge route. These nanostructures were synthesized by controlling the synthesis parameters such as current, voltage, catalyst, gas pressure etc. The structural, morphological and vibrational properties were investigated using X-ray diffraction, transmission electron microscopy, scanning electron microscopy, nitrogen adsorption-desorption isotherms and Raman Spectrometer. Both bright and dark field imaging were performed in order to study the morphological characteristics of the nanostructures. These images confirm the formation of high aspect ratio nanostructures of Si with diameters of up to 15 nm and lengths in the range of 500 – 1000 nm. Diffraction patterns were recorded to identify the number of phases formed and determine the crystal structure of the observed phases. The BET surface area of Si nanoparticles and high aspect ratio Si nanostructures (nanowires and nanotubes) are about 60 m^2/g and 360 m^2/g respectively. Raman spectrum of nanostructured Si showed both shift in the peak position and broadening of the Raman peak.

1. INTRODUCTION

In recent years, there is a renewed interest on the development of nanostructured silicon (Si) to advance the preparation of next generation energetic formulations. Two significant achievements that spurred this interest were the demonstration of (i) the preparation of a explosive composite based on porous Si filled with gadolinium nitrate ($Gd(NO3)_3$) in 2002. [Mikulec et al, 2002] and (ii) explosive reaction of nanoporous silicon immersed in cryogenic oxygen discovered in 2001. [Kovalev et al, 2001]. The growing interest in porous silicon is attributed to its high reactivity with oxygen owing to high internal surface area and higher energy of the exothermic reaction of silicon and oxygen than that of the most common carbon-based explosives. [Clément et al, 2005] Therefore, it is envisaged that the energetic compositions based on silicon will be extremely useful in several applications including in microarray analysis, as a smart ignition system for conventional explosives or as a propulsion system for microelectromechanical systems (MEMS) Moreover the energetic mixture prepared with silicon nanostructures is thermally more stable because of its higher melting point as compared to Al. The energetic formulation based on nano Si is also relatively more ESD insensitive.

These scientific developments motivated us to produce silicon nanostructured powder in our laboratory. In this paper, we report the preparation and characterization of silicon nanostructured powder using DC arc-discharge system, in particular, with an emphasis on the production of high aspect ratio Si nanostructures such as nanowires and nanotubes. Silicon nanotubes and nanowires with large surface area and high mechanical strength are likely to be a better choice of fuel compared to porous silicon and silicon nanoparticles. In this work, iron was used as a metal catalyst to prepare nanowires and nanotubes.

2. EXPERIMENTAL

2.1 Materials

Silicon wafers were crushed into powders and used as a precursor in the synthesis process. Iron powder with particle size less than <10 μm and purity of 99.9+ % obtained from Sigma Aldrich (product number: 267953) was used as the catalyst.

2.2 Synthesis of Si Nanostructured Powder

An attempt to grow high aspect ratio Si nanomaterials is described below. This was accomplished through the use of the plasma arc discharge reactor similar to those used for fullerene and nanotube synthesis.

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A graphite cup 3” in diameter and 7/8” in height was filled with a feedstock consisting of crushed silicon wafer and iron powder acting as catalyst for the growth of high aspect ratio Si nanostructures. Typically, three parts crushed silicon powder mixed with one part iron powder were used as the precursor in the arc-reactor. In some of the experiments, crushed Si powder was used without iron powder to understand the role of iron in the synthesis of Si nanostructures. The cathode was a ¼” diameter pure tungsten electrode. The reactor chamber was water-cooled during the entire duration of discharge.

The typical parameters used in the reactor operation were in the range of 25 – 75 A of current, 20-30 V and at a pressure of 40-100 kPa of Argon. These parameters were varied in an attempt to optimize the synthesis process for realizing high aspect ratio Si nanostructures.

2.3 Preparation of Energetic Mixtures

Accurately weighed 0.2 g of CuO nanorods and Si nanopowder were mixed together at an equivalence ratio of 1.6 in 2-propanol. The mixture was sonicated in an ultrasonic bath (Fisher 8835) for 6-8 hrs. The slurry was dried at 95^{o}C for 15 min to obtain powder.

2.4 Material Characterization

A variety of analytical tools were employed to investigate the fundamental structural, morphological and vibrational characteristics of the obtained Si nanostructured powder. X-ray diffraction and electron diffraction experiments were performed to determine the crystalline nature of the sample and indirect estimation of the chemical composition through the determination of lattice parameters. A Ultima IV Rigaku X-ray diffractometer was used in X-ray difftaction measurements. Both bright and dark field imaging was performed using a high resolution transmission electron microscope (Model: JEOL JEM 2000FX operated at 200 kV and Philips (FEI) EM420T (Tungsten Emitter) operated at 120 kV. X-ray Energy-Dispersive Spectroscopy (EDS) was also simultaneously performed to determine the composition. A scanning electron microscope (SEM) (Model: Hitachi S-4700) was also used to determine the morphological characteristics of the sample.

Nitrogen adsorption–desorption isotherms were measured using a Quantachrome Autosorb-1 automated gas sorption system and the surface areas were computed using the Brunauer–Emmett–Teller (BET) method. Raman measurements were performed using Renishaw inVia spectrometer system equipped with Hg Arc Lamp illumination with 360nm excitation and >400nm collection and an Argon Ion laser (20mW) excitation, at 514nm.

2.5 Reactivity Measurements

Reactivity measurements were performed by measuring the pressure generated as a function of time during the combustion propagation. Typically, a sample of 20mg powder was loaded in a cylindrical metal well (diameter – 6.25 mm and depth – 2mm) for each test. Ni-alloy fuse wire with a diameter of 0.13mm was used for the ignition of nanothermite material and this wire was in direct contact with the nanothermite.

Piezoelectric based pressure sensor (PCB Piezotronics Model 119B12, fastened to a rigid steel holder. was mounted directly on the top of the milli-well pre-loaded with the nanothermite material. The entire system was secured together by a rigid clamp and thus reducing the pressure leakage to the maximum extent. The thermite material was ignited by step applying DC voltage by SCR controlled capacitor discharge firing block. After blowing fuse wire the combustion process was recorded by pressure sensor. Pressure measurement error with this calibration procedure is within ± 10%.

The ESD sensitivity tests of these samples were performed using a measurement system fabricated by Electro-Tech Systems (ETS) Inc. Typically 2 - 4 mg nanopowdered thermite was placed in the sample holder. The sample is charged and discharged at 5000 V with varying capacitance values to obtain different energies and the number of charging/discharging cycles used in the present measurement is 24. A sample is considered ESD pass if it did not ignite upon charging. This means that the sample passes at all ESD energies equal or below the values.

3. RESULTS AND DISCUSSION

The synthesis process of Si nanostructures, the reactor was closely monitored during the synthesis process to adjust the distance between the cathode and the anode. Fumes were observed coming out of the graphite cup, indicating the evaporation of Si charge. Depending on the DC arc operation parameters used, the color of the resultant product varied. When a high current above 75A was used in the synthesis, the obtained powder was more blackish in color. This sample is found to contain carbon and copper impurities owing to the partial melting of the electrode assembly. When a current of 40-50 A was used in the synthesis, the color of the obtained powder was dark greenish with a slight yellowish shade. If iron powder was not used, the resultant color is more yellowish. Different colors of the obtained Si nanostructures indicated that it could be related to the composition and the various morphologies formed. Therefore, it is necessary to optimize the synthesis parameters to realize tunable nanostructured powder with

a specific morphology. It was observed that with an arc current of 40-50 A, sheets of material could be peeled off

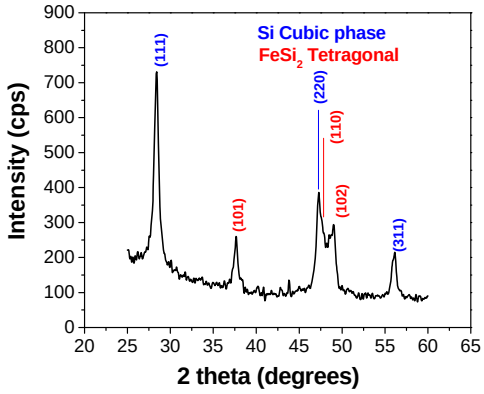

Figure 1. *Typical X-ray diffractiogram of Silicon nanostructured Powder*.

from the walls of the reactor indicating the formation of fibrous material. Visual observation of individual pieces of this material shows a relatively high strength.

3.1 Crystal Structure

Figure 1 shows a typical wide angle X-ray diffractogram obtained for Si nanostructured powder produced with parameters, I = 50 A, voltage = 25 V and 1:3 weight ratios of iron to Si powder in Ar ambient. It is evident that the sample is predominantly crystalline in nature. The observed peak positions were compared with those of powder diffraction files maintained by Joint Committee on Powder Diffraction Standards (JCPDS). The X-ray diffraction measurement revealed that the sample consists of essentially two crystalline phases – (a) Si and (b) $FeSi_2$. The crystal structure of Si phase is cubic diamond with a lattice constant of 5.43 Å while that of $FeSi_2$ is tetragonal with a = b = 2.69 Å and c= 5.14 Å. This finding was confirmed from electron diffraction pattern also as will be shown in the next section. The broadened diffraction peaks indicate the reduced dimensions of the Si nanopowder formed with DC arc-discharge.

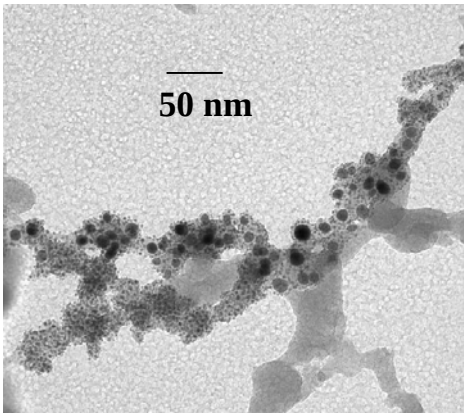

Figure 2. *Typical Bright Field TEM image recorded for Si nanoparticles.*

3.2 Morphological Characteristics

Detailed imaging of the obtained Si nanostructured powder facilitated their morphological properties such as their shape and dimensions. The typical image recorded for Si nanopowder formed with arc reactor parameters of 25A and 30V without using iron as catalyst shown in Figure 2 reveals that the morphology of the Si nanopowder is spherical nanoparticles with a size distribution in the range of 5- 40 nm.

Since the objective was to prepare high aspect ratio Si nanostructured powder, the current was increased to 40A. The typical TEM images of the observed nanostructured powder are shown in Figure 3. These images suggest that the morphology of the produced nanostructured powder consists of a possible mixture of nanotubes and nanowires with diameters of up to 15 nm and lengths in the range of 500 – 1000 nm as shown in Figure 3(a) and Figure 3(b). From the selected area electron diffraction (SAED) pattern, it was found that the core is essentially crystalline Si phase and the shell is amorphous SiO_2. From the image 3(a), the diameter of the core is 3-5 nm and that of the shell is 5-7 nm. Thus, it is clear that optimization of synthesis parameters and surface passivations are essential to control the perpetual oxidation of Si nanowires.

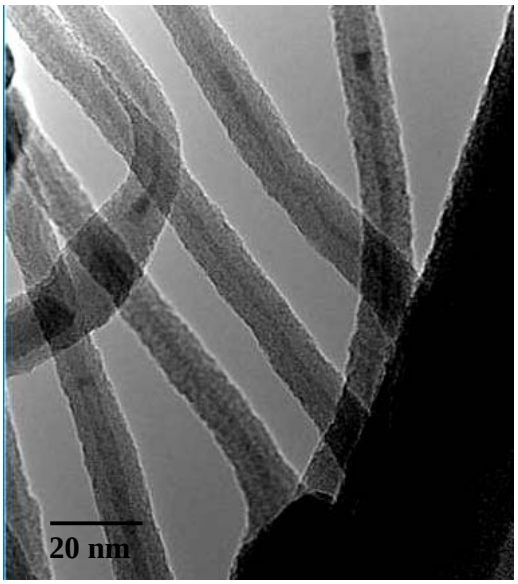

Figure 3(a) *A bright field TEM micrograph showing core (Si)- shell (SiO_2) nanowires.*

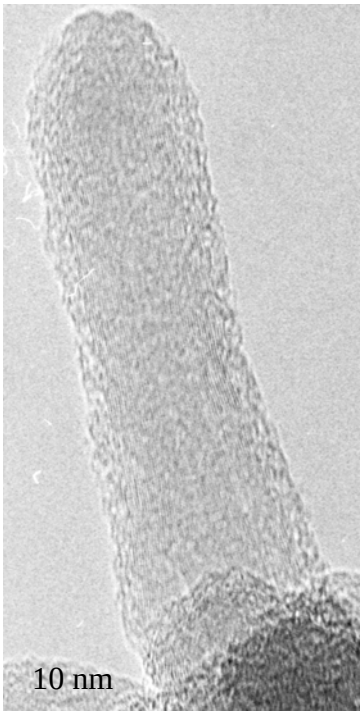

Figure 3(b) *High Resolution Image showing the lattice planes in nanotube*

Figure 3(b) shows a high resolution image of a single Si nanotube showing the lattice planes in Si. It is observed that in case of Si nanotubes, the oxide layer shell thickness is 1-2 nm. The analysis of the HRTEM pattern leads to a spacing of 0.31 nm. This spacing could correspond to the separation distance between the {111} planes in crystalline Si as reported in literature. [Perepichika et al, 2006] This confirms that the nanotube is indeed Si. However, if the surface dangling bonds are not satisfied, the surface is prone to undergo perpetual oxidation.

However, it must be emphasized that hydrogen terminated Si surfaces is expected to serve better in nanoenergetics applications. Therefore, it is necessary to develop suitable post-processing methods to control the thickness of the oxide layer. It will be interesting to passivate the surface dangling bonds of the freshly prepared Si nanostructures by treating them with a mixture of HF and ethanol. Such treatments are expected to the removal of native oxide layer and provide a closed hydrogen cover as reported in literature. [Koch et al, 2007].

Also, annealing at higher temperature in a partial atmosphere of O_2/Ar could help to satisfy surface dangling bonds. Some published reports on porous Si suggest that the hydrogen atoms covering the Si atoms at the surface remain unaffected during this annealing. [Koch et al, 2007] We are working on the problem of chemical stability of Si against natural aging by oxidation in order to implement Si as a fuel in energetic formulations.

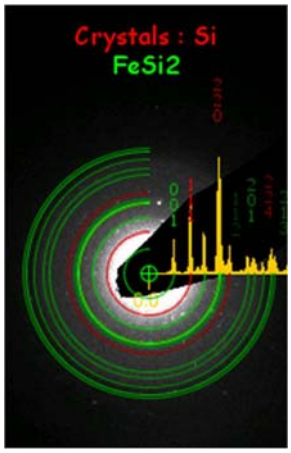

Figure 4. *Superimposed SAED pattern recorded from a collection of nanowires and nanotubes.*

The electron diffraction pattern from a collection of nanotubes and nanowires recorded at a low magnification is shown in Figure 4. The theoretical intensities of the each of the rings representing a set of {hkl} planes are also shown as a function of the distance from the center spot. Based on the analysis of this pattern, the nanostructured sample essentially consists of two phases – cubic Si and tetragonal FeSi2. Only the major peak intensities are identified to make the pattern clear. Thus, this result is found to confirm the analysis from X-ray diffraction pattern shown in Figure.1.

The chemical composition of a single nanowire was measured from EDS attached to the TEM is shown in Figure 5. The red circle in the bright field image of Figure 5 indicates the region on a single nanowire where the electron beam was focused to collect the EDS data. The observed spectrum shows that the X-rays originate from the presence of carbon, copper, oxygen and Si. Copper and carbon peaks are attributed to the carbon coated copper grid on which the specimen was prepared. The Si and the O peaks are attributed to the sample. The spectrum shows relatively low intensity peak of oxygen in comparison with that of Si. From the data obtained from SAED patterns and the elemental composition obtained from EDS measurement, it is clear that the nanowire is comprised of Si core and a SiO_2 shell.

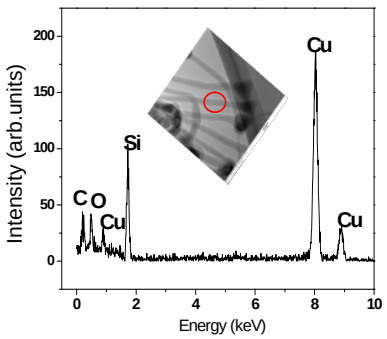

Figure 5 *EDS composition measurement from a single nanowire.*

3.3 Surface Area Measurements

The measured nitrogen adsorption isotherms of Si nanoparticles and that of a sample consisting of a mixture of nanowires and nanotubes are shown in Figure 6(a). The BET plots from the analysis of the nitrogen adsorption-desorption isotherms shown in Figure 6(b) shows that the surface area of Si nanoparticles with a size range of 5 – 40 nm is about 60 m^2/g while that of high aspect ratio Si nanowires and Si nanotubes is about 360 m^2/g. This surface area value obtained for the sample consisting of a mixture of Si nanotubes and Si nanowires is very close to the typical values reported for single

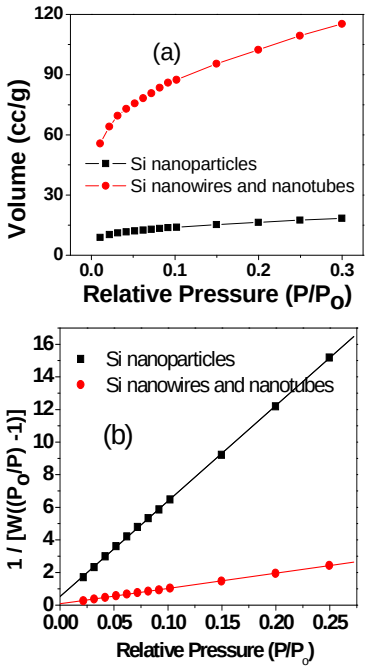

Figure 6 ***(a)*** *Nitrogen adsorption isotherms and* ***(b)*** *BET plots for surface area determination.*

walled carbon nanotubes. The high surface area of Si nanostructures indicates that the morphology of the sample is quite homogeneous.

3.4 Raman Measurements

Raman measurements of this nanostructured powder were carried out and the data was compared with that of the measured spectrum of bulk silicon performed under identical experimental conditions. These spectra are shown in Figure 7.

The shift in the peak from 522 cm^{-1} for bulk sample to 512 cm^{-1} for the high aspect ratio silicon nanostructures and broadening of the full width at half

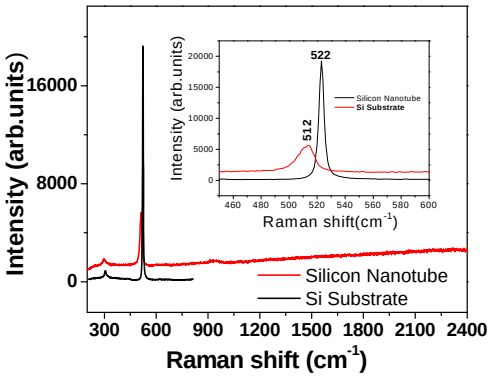

Figure 7. *Raman Spectrum of Silicon Nanotube and bulk Silicon*

maximum (FWHM) spectrum from 4 cm^{-1} for bulk to 12 cm^{-1} is probably due to the quantum confinement effect. The Raman spectrum of silicon nanotube also shows the presence of two peaks at 295 cm^{-1} and 935 cm^{-1} from the second-order transverse acoustic phonon mode (2TA) and second-order optical phonon mode (2TO), respectively. Presence of these second order peaks is indicative of highly ordered structures.

3.5 Reactivity and ESD Measurements

Preliminary experiments were carried out by mixing Si nanostructured powder as a fuel and copper oxide as an oxidizer to form an energetic mixture. A photograph taken during the combustion of CuO-Si based energetic mixture mixed with an equivalence ratio of 1.6. is shown in Figure 8. The mixture shows a very good ability to sustain self-propagating combustion phenomenon. Pressure generated as a function of reaction time was monitored using the experimental set-up described in Figure 9. The measured peak pressure and the pressurization rate are 7.5 MPa and 0.01 MPa/µs. The reaction is extremely slow and the reaction takes 1 ms to complete. The measured ESD energy (pass) of this

energetic mixture is 16 mJ which shows the reduced sensitivity to ESD event in comparison with that of other nanothermites such as CuO-Al, Bi_2O_3-Al, WO_3-Al etc.

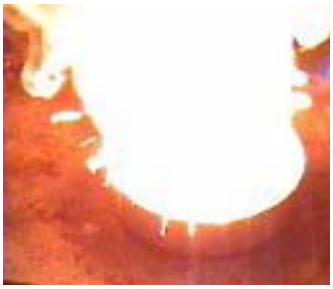

Figure 8 *Combustion of an energetic mixture consisting of Si nanopowder and CuO nanorods.*

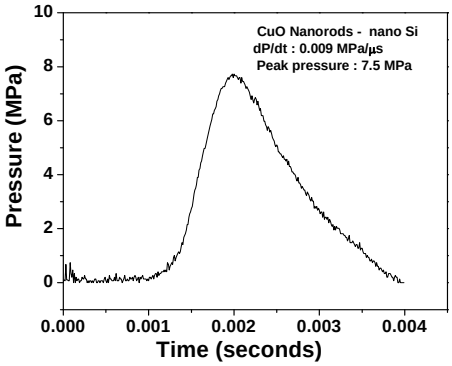

Figure 9. *Reactivity of nanosttructured Si with CuO nanorods.*

3.6 Future Perspective of Si Nanostructures in Energetics

It is expected that mixing traditional metal oxides like CuO, Bi_2O_3, WO_3 etc with high aspect ratio Si nanostructures is likely to produce energetic composites with high energy yield with reduced ESD sensitivity, which may lead to exciting pyrotechnic applications. Controlling the oxide layer thickness as well the amount of iron catalyst is extremely important to achieving the desired energetic properties. Thus, attempts are presently underway to prepare high aspect ratio Si nanostructured material without Fe nanoparticles as catalysts or very small amounts of Fe to reduce the dead mass in the energetic mixtures. It is visualized that these high aspect ratio silicon nanowires or nanotubes can be decorated on the external surface or filled with explosive nanoparticles such as ammonium nitrate or RDX nanoparticles to realize next generation novel explosive nanoenergetic formulations.

4. CONCLUSION

Our work demonstrates the preparation of high aspect ratio Si nanostructures using Fe as catalyst using DC arc discharge method. These high aspect ratio Si nanostructures include nanotubes and core-shell Si nanowires. These nanostructures were extensively characterized using a variety of analytical techniques such as X-ray diffraction, TEM, SEM, EDS, nitrogen adsorption-desorption isotherms, and Raman spectroscopy. The high aspect ratio nanostructures show high crystalline quality and the typical lengths and the diameters are upto 1000 nm and 15 nm respectively. The samples were found to be very homogeneous. The XRD and the SAED patterns agreed with each other and the crystalline phases identified in the mixture are cubic diamond Si and tetragonal $FeSi_2$. The surface areas of Si nanoparticles and that of a sample consisting of a mixture of Si nanotubes and nanowires are 60 m^2/g and 360 m^2/g respectively. The combustion of an energetic mixture consisting of Si nanopowder and CuO nanorods is found to sustain self-propagation. Further work is in progress to assemble externally on the surface of high aspect ratio Si nanostructured powder and/or infiltrate low grade explosive nanoparticles like ammonium nitrate, ammonium perchlorate etc into the nanotubes to advance the synthesis of novel energetic materials.

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